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Two-dimensional frameworks built from Single-Molecule Magnets

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networks; complexes; clusters; family; dimer; units

Abstract

Fine tuning the Mn / salicylaldoxime / trimesic acid reaction conditions leads to the formation of a regular 2D net held together by dative bonds and to a non-regular 2D net stabilised by both dative and hydrogen bonds. Both networks are built from [Mn_6] Single-Molecule Magnets.

Introduction

Since it has been established that the physical properties of crystalline molecular materials can be influenced by crystal packing effects and intermolecular interactions (*e.g.* hydrogen bonding, $\pi\cdots\pi$ interactions *etc*), we and others have been investigating how to manipulate the magnetic properties of Single-Molecule Magnets (SMMs) in the solid state by modulating their surroundings.[1] To this end, we recently exploited certain members of a family of hexanuclear, [Mn_6], and trinuclear, [Mn_3], Mn^{III} complexes of general formulae [$Mn^{III}_6O_2$(R-sao)$_6$(O_2CR)$_2$(L)$_{4-6}$] and [Mn^{III}_3O(R-sao)$_3$(X)(L)$_3$] ($saoH_2$ = salicylaldoxime; R = H, Me, Et *etc*; X = RCO_2^-, ClO_4^-; L = solvent)[2-3] as building blocks for constructing discrete and infinite supramolecular architectures with the use of both bis-pyridyl[4] and bis-carboxylate[5] type ligands. Both types of bridging ligands resulted in, among others, coordination polymers built from either [Mn_3] or [Mn_6] clusters. The bis-pyridyl type ligands gave rise to both one- (1D) and two-dimensional (2D) coordination polymers based on [Mn_3] SMMs while the bis-carboxylate ligands resulted in 1D coordination polymers incorporating [Mn_6] SMMs.[4,5]

Having in mind that the incorporation of bis-carboxylate ligands resulted in polymeric species where the [Mn_6] clusters retained their single molecule behaviour, we sought to construct higher dimensionality coordination polymers (*i.e.* 2D or 3D) built from [Mn_6] SMMs and polycarboxylate ligands. For this purpose, we incorporated 1,3,5-benzene-tricarboxylic acid (trimesic acid, $tmaH_3$) into blends of manganese / $saoH_2$ reaction mixtures to isolate the 1D coordination polymer [Mn_6O_2(sao)$_6$(tmaH)(MeOH)$_{8.5}$(H_2O)$_{0.5}$]·(MeOH)$_{0.75}$(H_2O)$_{0.125}$ **1**·(MeOH)$_{0.75}$(H_2O)$_{0.125}$ and the 2D coordination polymer [Mn_6O_2(sao)$_6$(tma)$_{0.66}$(MeOH)$_{3.33}$(H_2O)$_{1.33}$]·(MeOH)$_{4.46}$(H_2O) **2**·(MeOH)$_{4.46}$(H_2O). Both polymers are constructed from [Mn_6] SMM building blocks. Besides the efforts to intentionally link SMMs or magnetically interesting clusters, higher dimensionality (i.e. 2D, 3D) polymers are scarce.[6] Complex **2** represents a rare 2D framework constructed intentionally from SMMs building blocks.

Although it is possible to employ pre-formed [Mn_6] and [Mn_3] species as starting materials for the synthesis of polymeric materials [they are solution stable as gauged by NMR, mass

spectrometry and solution SQUID magnetometry[7]], it is much more efficient to simply perform the reactions *in situ*. The $Mn(ClO_4)_2 \cdot 6H_2O$ / $saoH_2$ / $tmaH_3$ / base reaction blend is however very sensitive to reaction conditions and indeed it produces different complexes depending on the order of addition of the reagents. The 1D coordination polymer **1** is produced when $tmaH_3$ is added into an alcoholic solution containing $Mn(ClO_4)_2 \cdot 6H_2O$ / $saoH_2$ / MeONa, while the 2D coordination polymer **2** is formed when MeONa was added into an alcoholic solution containing $Mn(ClO_4)_2 \cdot 6H_2O$ / $saoH_2$ / $tmaH_3$. Complex **1** was isolated serendipitously during our efforts to synthesise the targeted 2D coordination polymer **2**.

Complex **1** (Figure 1) crystallises in the triclinic space group $P\bar{1}$.‡ The assymetric unit consists of two $tmaH^{2-}$ anions, one $[Mn^{III}_6]$ and two $[Mn^{III}_3]$ units.† In effect, there are two crystallographically independent $[Mn_6]$ clusters, namely $[Mn_6]_A$ and $[Mn_6]_B$, repeating along the chain of **1**. Each $[Mn_6]$ unit consists of two off-set, stacked $[Mn^{III}_3O(sao)_3]^+$ triangles linked by two oximato O-atoms, while one phenolato O-atom bridges between the $[Mn_3]$ subunits in $[Mn_6]_A$. Four sao^{2-} ligands bridge along the edges of the $[Mn_3]$ subunits in a $\mu_3:\eta^1:\eta^1:\eta^2$ fashion, one in a $\mu_3:\eta^2:\eta^1:\eta^1$ fashion while the remaining seven sao^{2-} ligands adopt the $\mu:\eta^1:\eta^1:\eta^1$ coordination mode. Ten out of the twelve crystallographically independent Mn^{III} atoms are in an (axially) elongated octahedral environment with one Mn^{III} in each of the $[Mn_6]$ clusters being five-coordinate and in a square pyramidal environment. Nine MeOH molecules (one is 50% disordered with a H_2O molecule) occupy the Jahn Teller positions on the Mn^{III} ions, with the remaining sites coordinated by carboxylato O-atoms from the two crystallographically independent $tmaH^{2-}$ ligands. These ligands adopt the $\mu_4:\eta^1:\eta^1:\eta^1:\eta^1$ and $\mu_3:\eta^1:\eta^1:\eta^1$ coordination modes, respectively. The Mn-N-O-Mn torsion angles for $[Mn_6]_A$ are 32.55° for Mn4-N-O-Mn5, 38.22° for Mn5-N-O-Mn6, 21.47° for Mn6-N-O-Mn4, 41.83° for Mn7-N-O-Mn8, 12.25° for Mn8-N-O-Mn9 and 30.13° for Mn9-N-O-Mn7. For $[Mn_6]_B$ the corresponding angles are 18.00° for Mn1-N-O-Mn2, 8.18° for Mn2-N-O-Mn3, 13.44° for Mn3-N-O-Mn1, 15.99° for Mn10-N-O-Mn11, 9.05° for Mn11-N-O-Mn12 and 18.44° for Mn12-N-O-Mn10.

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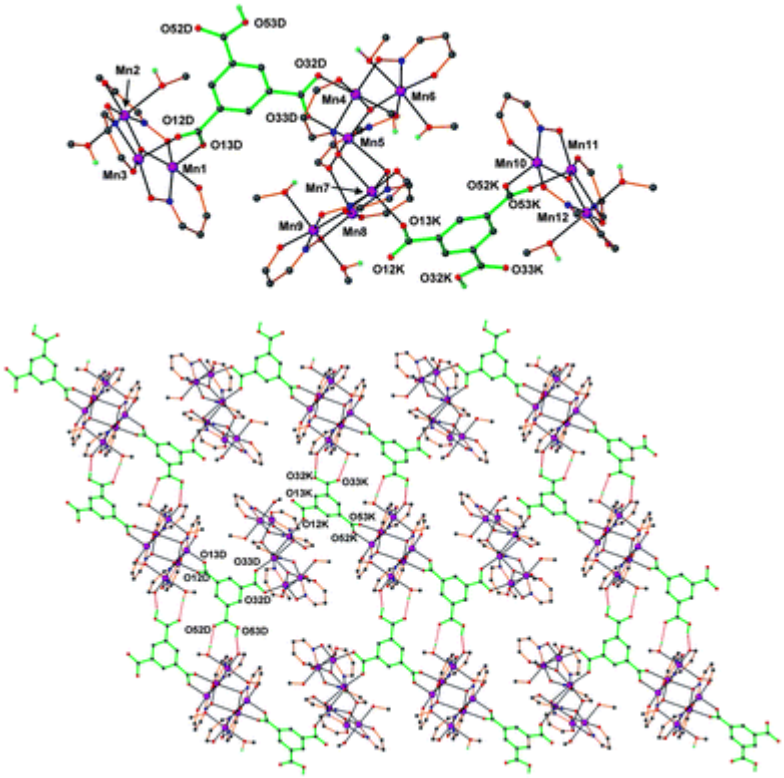

Figure 1. (top) The asymmetric unit of complex **1**. (bottom) The hydrogen-bonded chains of complex **1** creating a non-regular 2D framework. Most hydrogen atoms and some carbon atoms of the sao^{2-} ligands have been omitted for clarity. Colour code: Mn: purple, O: red, N: blue, C: grey, H: cyan.

The chains of **1** are arranged in parallel, with the free carboxylic acid groups of the $tmaH^{2-}$ ligands able to donate a hydrogen bond to a phenolato O-atom and accept a hydrogen bond from a neighbouring coordinated MeOH molecule, thus bridging between chains to create a 2D non-regular network (Fig. 1) with vertex symbol (4.6^2;4.6.4.6). The $tmaH^{2-}$ ligands and the $[Mn_6]_B$ clusters serve as 3- and 4-connected nodes within the 2D network, respectively, with $[Mn_6]_A$ simply bridging between the $tmaH^{2-}$ ligands.

Complex **2** also crystallises in the triclinic space group $P\bar{1}$.‡ The assymetric unit consists of one tma^{3-} anion and three $[Mn^{III}_3O(sao)_3]^+$ subunits (Fig. 2).† This arrangement gives rise to three crystallographically independent $[Mn_6]$ clusters, with each sitting on an inversion centre. Two off-set stacked $[Mn^{III}_3O(sao)_3]^+$ triangles linked by two oximato O-atoms create each $[Mn_6]$ cluster. Therefore, four sao^{2-} ligands bridge along the edges of the $[Mn_3]$ subunits in a $\mu:\eta^1:\eta^1:\eta^1$ fashion, while two sao^{2-} ligands adopt the $\mu_3:\eta^1:\eta^1:\eta^2$ coordination mode. Two Mn^{III} ions in each $[Mn_6]$ are five-coordinate in a square pyramidal environment while the remaining four Mn^{III} ions are in an (axially) elongated octahedral environment. Ten MeOH and four H_2O molecules, ten carboxylate O-atoms from the tma^{3-} ligands and six oximato O-atoms from the sao^{2-} ligands

occupy the Jahn Teller positions on the Mn^{III} ions. The tma^{3-} ligand bridges five Mn^{III} ions, from three different [Mn_6] clusters, adopting the $\mu_5:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1$ coordination mode. The Mn-N-O-Mn torsion angles are 9.45° for Mn1-N-O-Mn2, 1.81° for Mn2-N-O-Mn3 and 31.37° for Mn3-N-O-Mn1 for the first [Mn_6], 24.64° for Mn4-N-O-Mn5, 14.67° for Mn5-N-O-Mn6 and 18.22° for Mn6-N-O-Mn4 for the second [Mn_6] and 2.33° for Mn7-N-O-Mn8, 29.81° for Mn8-N-O-Mn9 and 22.60° for Mn9-N-O-Mn7 for the third [Mn_6].

The [Mn_6] clusters and the tma^{3-} ligands assemble to create a regular 2D network with a (6,3) topology, commonly known as a honeycomb, with the tma^{3-} ligands serving as 3-connected nodes and the [Mn_6] clusters as the spacers (Fig. 2).

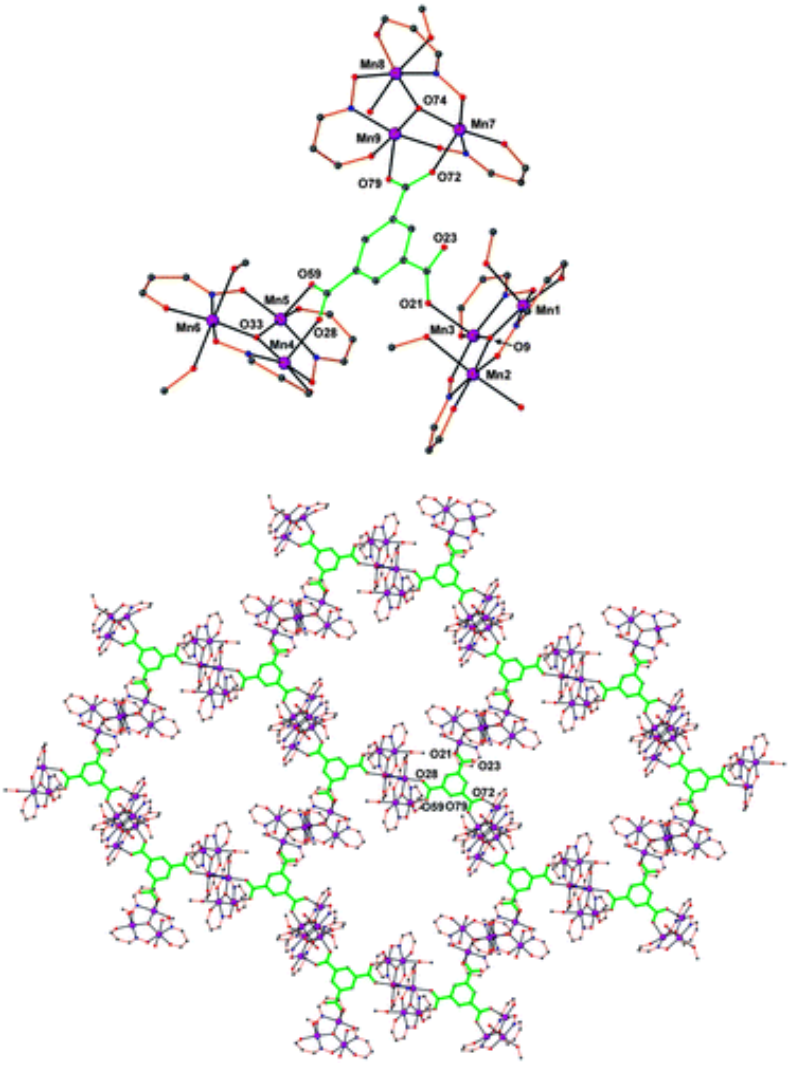

Figure 2. (top) The asymmetric unit of complex **2**. (bottom) The 2D framework of complex **2**. All hydrogen atoms and many carbon atoms of the sao^{2-} ligands have been omitted for clarity. Colour code as in Figure 1.

Previous studies of molecular salicylaldoxime-based [Mn^{III}_6] and [Mn^{III}_3] clusters have shown that their magnetic behaviour is strongly correlated to small geometrical changes. Specifically, the sign and magnitude of the exchange (J) between neighbouring Mn^{III} ions is dependent on the Mn-N-O-Mn torsion angle. Unfortunately the presence of more than one crystallographically independent [Mn_6] in the crystal structures of both **1** and **2**, which possess different geometries, precludes a detailed *quantitative* analysis of the magnetic behaviour.

Solid state dc magnetic susceptibility data for **1** and **2** were recorded between 275 and 5 K in an applied field of 0.1 T. The plots of $\chi_M T$ versus T for **1** and **2** are shown in Fig. S1. The $\chi_M T$ products at 275 K are 16.54 and 14.95 $cm^3\ mol^{-1}\ K$ for **1** and **2**, respectively, close to the spin-only ($g = 2$) value of 18 $cm^3\ mol^{-1}\ K$ expected for a [Mn_6] unit comprising six high spin Mn^{III} ions. The $\chi_M T$ values for both complexes remain approximately constant as the temperature is lowered, before dropping more rapidly at temperatures below 125 K. Thereafter, the $\chi_M T$ value for complex **1** decreases constantly to reach a value of 9.1 $cm^3\ mol^{-1}\ K$ at 5 K, while that for complex **2** decreases to a value of ~8.0 $cm^3\ mol^{-1}\ K$ at 20 K and then plateaus to 5 K. The decrease of the $\chi_M T$ product upon cooling to smaller but non-zero values is consistent with the presence of both antiferromagnetic and ferromagnetic interactions between the Mn^{III} ions with the low-temperature values indicating $S \approx 4$ spin ground states for the [Mn^{III}_6] units in both complexes. Indeed we note that the $\chi_M T$ behaviour for **1** and **2** is very similar to that observed for previously reported and magnetically isolated [Mn^{III}_6] complexes with $S = 4$ spin ground states. For comparison we include in Figure S1 the data for [$Mn_6O_2(sao)_6(ketoacetate)_2(EtOH)_2(H_2O)_2$] (**3**) and [$Mn_6O_2(sao)_6$(1-Me-cyclohex)$_2(MeOH)_4$] (**4**) from reference 3c which contain [Mn_6] with similar Mn-N-O-Mn torsion angles. In order to investigate the possibility of long range antiferromagnetism we performed zero field ac susceptibility measurements on **1** and **2** in the 1.8 – 10 K temperature range with a 3.5 G ac field oscillating at frequencies ranging from 50 – 1000 Hz (Fig. 3). A cusp in the real component χ' (Fig. S3) is accompanied by a non-zero imaginary component χ'' at ~3 K. The maxima for both are strongly frequency dependent, suggesting super-paramagnetic blocking of the magnetisation. Arrhenius plots (inset Fig. 3) constructed from the χ'' data afford $\tau_0 = 3.3\times10^{-9}$ s and $U_{eff} = 32.84$ K (22.82 cm^{-1}) for **1**, and $\tau_0 = 5.6\times10^{-8}$ s and $U_{eff} =$ 24.54 K (17.05 cm^{-1}) for **2**. The presence of *significant* inter-[Mn_6] interactions would be expected to slow down the spin dynamics at low temperatures and this would be manifested in a smaller frequency shift, k. Using the average values of blocking temperatures (T_B) of 2.70 K for **1** and 2.69 K for **2**, the frequency shift of T_B is calculated as $k = \Delta T_B/(T_B \Delta \log f)$, where ΔT_B is the change in T_B for the given change in frequency $\Delta \log f$, were $\Delta \log f = 1.30$ for both complexes. This provides values of 0.19 and 0.24 for **1** and **2**, respectively, which are within the range expected for super-paramagnets and close to those reported for molecular [Mn_6] complexes. This suggests that the relaxation is in accordance with SMM behavior, and is not attributed to long

range interactions mediated through the polycarboxylate ligands.

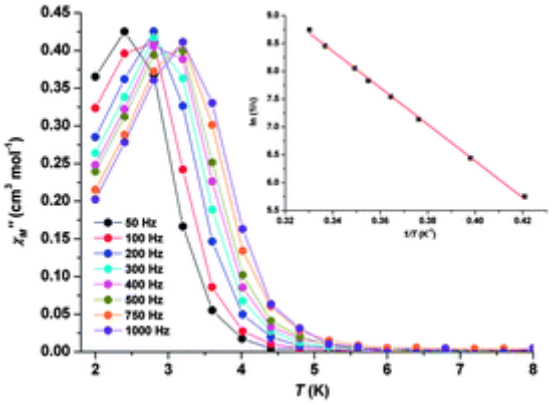

Figure 3. Plot of χ'' versus T for complex **1** at the indicated temperature and frequency ranges. Inset: Arrhenius plot constructed from the χ'' data to afford $\tau_0 = 3.3\times10^{-9}$ s and $U_{eff} \approx 33$ K.

To conclude, we presented two new coordination polymers built from [Mn_6] clusters and trimesate anions. The first polymer conforms to a non-regular 2D net held by both dative and hydrogen bonds, while the second adopts a regular 2D net held together exclusively by dative bonds. Both polymers consist of magnetically isolated [Mn_6] SMMs with $S \approx 4$ ground states. We continue exploiting [$Mn_{3/6}$] SMMs as starting materials for the construction of polymeric molecular magnetic materials with the next stage being to introduce added functionality through the presence of redox-active or radical linker ligands which might enable [stronger] communication between the cluster building blocks.

Notes and references

‡ Crystal data for **1**: $C_{224}H_{220}Mn_{24}N_{24}O_{101\cdot50}$, M = 6190.80, triclinic, a = 12.5838(4) Å, b = 19.5656(5) Å, c = 25.6050(6) Å, α = 99.792(2)°, β = 90.436(2)°, γ = 97.756(2)°, V = 6152.5(3) Å^3, T = 100(2) K, space group $P\bar{1}$, Z = 1, 121047 reflections measured, 24245 independent reflections (R_{int} = 0.1296). The final R_1 values were 0.0674 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1494 ($I > 2\sigma(I)$). The final R_1 values were 0.1601 (all data). The final $wR(F^2)$ values were 0.1759 (all data). Crystal data for **2**: $C_{83\cdot70}H_{100\cdot80}Mn_9N_9O_{42\cdot20}$, M = 2402.52, triclinic, a = 14.7534(4) Å, b = 16.3686(4) Å, c = 22.2983(6) Å, α = 101.659(2)°, β = 101.396(2)°, γ = 96.649(2)°, V = 5101.3(3) Å^3, T = 100 K, space group $P\bar{1}$, Z = 2, 42686 reflections measured, 19808 independent reflections (R_{int} = 0.055). The final R_1 values were 0.0744 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0128 ($I > 2\sigma(I)$). The final R_1 values were 0.1160 (all data). The final $wR(F^2)$ values were 0.0128 (all data).

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